

Remarkably small critical exponent for the viscosity of a polymer solution

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We have measured the apparent critical exponent γ characterizing the divergence of the viscosity $\eta \propto (T - T_c)^{-\gamma}$ near the liquid-liquid critical point of the mixture polystyrene in diethyl malonate. The data span the range in reduced temperature of $10^{-4} < (T - T_c)/T_c < 10^{-1}$. The sample was prepared from the same materials used by Gruner *et al.* in their capillary viscometer [Macromolecules **23**, 510 (1990)]; however our torsion oscillator viscometer had a shear rate 80 times lower. This increased the range of reduced temperatures where shear effects could be neglected. In spite of the large reduction in shear rate and the different viscometry technique, the parameters fitted to our data and those of Gruner *et al.* are in agreement. For this polymer solution, γ is in the range 0.028 ± 0.003 , close to recent results for two other polymer solutions measured in capillary viscometers. However, it is significantly smaller than the exponent for pure fluids (0.041 ± 0.001) and simple binary mixtures (0.042 ± 0.002). It appears that polymer solutions are in a dynamic universality class different from that of simpler fluids.

I. INTRODUCTION

As is the case for binary mixtures of simple liquids, the viscosity η of polymer solutions diverges asymptotically near the critical solution temperature T_c as

$$\eta \propto \epsilon^{-\gamma}, \quad (1)$$

where $\epsilon \equiv (T - T_c)/T_c$ is the reduced temperature. Recent experiments near the consolute points of four binary mixtures of small molecules¹ and near the liquid-vapor critical points of two pure fluids² found apparent critical exponents in the range $\gamma = 0.042 \pm 0.02$, confirming the widely accepted hypothesis that both types of fluids are in the same dynamic universality class. (See Ref. 3 for reviews.) Furthermore, this range of γ is consistent with the recent mode-coupling calculation by Hao.⁴

Light scattering (e.g., Refs. 5–8) and coexistence curve (e.g., Refs. 9 and 10) data for polymer solutions, as well as for pure fluids and simple binary liquids, are all consistent; thus all three types of fluids are in the same static universality class. In contrast, unique aspects of polymer behavior such as intramolecular contraction and intermolecular entanglement could possibly change the scaling of dynamic critical phenomena. Examples of dynamical behavior of semidilute polymer solutions differing from that of simpler fluids include nonexponential autocorrelation functions^{11,12} and qualitatively different responses to large shear rates.^{13–15} Recently, Tanaka and Miura¹⁶ presented measurements of the dynamic modulus of polystyrene in diethyl malonate and argued that the critical anomaly was suppressed by slow polymer dynamics. The results of the present work support the idea that polymer solutions are in a dynamic universality class different from that of simpler fluids.

In this paper, we report new measurements of the shear viscosity near the critical point of polystyrene in diethyl malonate which, when combined with previous measurements on the same system,¹⁷ achieve an unprecedented combination

of a wide range of temperature and, close to T_c , a low shear rate. A low shear rate is essential for measuring the hydrodynamic viscosity without encountering complications due to the fluid's characteristic internal relaxation. Near the critical consolute point of a polymer solution, the most important such effect can be due to concentration fluctuations, which relax more slowly than fluctuations in solutions composed only of small molecules. The fluctuation relaxation time τ depends on the correlation length ξ and the viscosity η :

$$\tau \approx \frac{6\pi\xi^3\eta}{k_B T_c}, \quad (2)$$

where k_B is Boltzmann's constant. At the same reduced temperature, both ξ and η are larger in polymer solutions than either in pure fluids or in solutions of small molecules. In pure fluids, the conditions of low frequency ($\omega\tau \ll 1$) and low shear rate ($\dot{\gamma}\tau \ll 1$), required for measuring the hydrodynamic viscosity, are easily met in the regime $\epsilon < 10^{-4}$. In binary liquid mixtures, the relaxation time is longer (order of 1 s at $\epsilon = 3 \times 10^{-6}$ or 1 mK from T_c), and it can lead to significant departures of the viscosity data from the low-frequency, low-shear rate limit. In the present polymer solution, the relaxation time is estimated to be 3 h at $\epsilon = 3 \times 10^{-6}$. Thus, even with our viscometer's low shear rate we could use data only at $\epsilon > 1.5 \times 10^{-4}$ (40 mK above T_c). Nevertheless, compared to measurements with typical capillary viscometers, this is ten times closer to T_c .

This investigation was motivated by the work of Gruner *et al.*,¹⁷ who used a capillary viscometer to measure the critical viscosity of polystyrene in diethyl malonate. They found the fitted value of the viscosity exponent to be sensitive to the choice of the function describing the noncritical, or background, viscosity, varying from $\gamma = 0.015$ to $\gamma = 0.060$. Because their maximum shear rate was 40 s^{-1} they tried both eliminating the data near T_c and applying theoretically motivated corrections. They were unable to find a function that

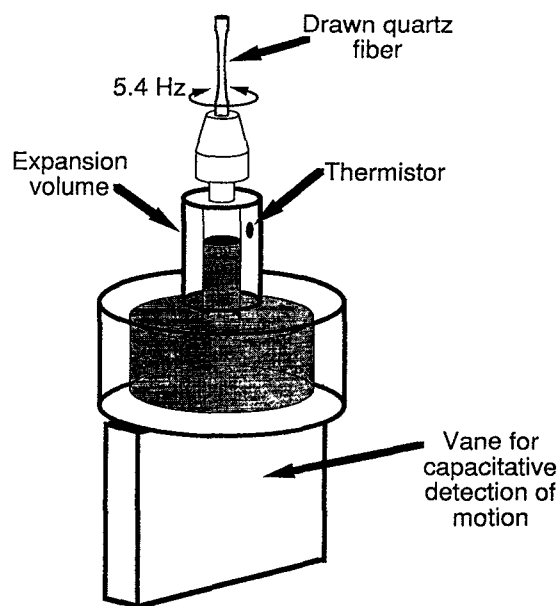


FIG. 1. The torsion oscillator consisted of a hollow stainless steel cylinder suspended by a drawn quartz fiber. Oscillations of the cylinder were damped by shear of the sample contained within. The sample volume and the dimensions of the expansion volume were chosen to allow data to be taken over a 30 K range with a negligible contribution to the decrement from the fluid in the expansion volume.

adequately described the full 91 K range of their data. Although the present technique and shear rate differ greatly from those used by Gruner *et al.*, we obtained similar results. In particular, for the 25 K range near T_c , both measurements yielded viscosity exponents in the range $\gamma = 0.028 \pm 0.003$. In contrast, the viscosity exponents measured in pure fluids and in binary mixtures of small molecules are approximately 1.5 times larger.

II. EXPERIMENTAL METHODS

A. Sample preparation

The polystyrene and diethyl malonate had been previously prepared for the viscosity measurements of Gruner *et al.*¹⁷ The polystyrene had a molecular weight of 1.02×10^5 and a ratio of weight-average to number-average molecular weights of 1.02. Two previously prepared solutions were blended in a glove box under dry nitrogen to obtain a mixture having a composition of 9.458 wt. % of polystyrene in diethyl malonate (Gruner *et al.* used 9.473%). The viscometer was loaded with 11.901 g of this mixture, an amount chosen to keep the liquid–air meniscus in the viscometer's expansion volume throughout the 30 K measurement range (see Fig. 1). The critical temperature was at 274.3 ± 0.2 K, about 1 K lower than that measured by Gruner *et al.* This 1 K difference in T_c indicates a very minor difference in contamination by water, which raises T_c .⁹ The critical temperature drifted by less than 10 mK during a period of three months. Weighing the filled viscometer showed that no significant leakage of the sample occurred during the ten

months following loading. Before beginning each run, the sample was mixed by removing the viscometer from its torsion fiber suspension and shaking the viscometer by hand for several minutes, causing the air bubble to move from the expansion volume throughout the viscometer's interior.

B. Apparatus and techniques

The torsion-oscillator viscometer was similar to the viscometers used for earlier measurements on pure fluids² and binary liquid mixtures.^{1,18} All of these viscometers had three features that are important for near-critical samples: (1) precise temperature control (<1 mK); (2) low frequency (~ 1 Hz); and (3) small oscillation amplitudes to achieve low shear rates ($0.1\text{--}1\text{ s}^{-1}$). The low frequency and shear rate are needed to remain in the hydrodynamic regime, and they also ensured that viscous heating was negligible.

As shown in Fig. 1, the fluid was contained in a cylindrical sample cell comprised of two stainless steel parts soldered together to create an internal volume of 11.4 cm^3 . The cylindrical extension to the main volume allowed for thermal expansion of the sample. The radius of the expansion volume was 3.18 mm, small enough that the fluid in this volume made a negligible contribution to the oscillator's decrement. The height was 13 mm, allowing free expansion of the sample over a 30 K range. A disk of PTFE sealed the sample, and a thermistor glued into the wall of the expansion volume measured the temperature of the viscometer. Added to the sample cell were a pin vise to grip the torsion fiber and an aluminum vane screwed onto the bottom.

As with the previous instruments,^{1,2,18} the viscometer oscillated in a thermostat comprised of three evacuated, nested, aluminum shells. The thermally isolated viscometer acted as a fourth, passive thermostat stage with excellent temperature stability. The viscosity measurements were made while the viscometer's temperature slowly relaxed towards the programmed temperature of the inner shell. Typically, the viscometer was cooled from 295 to 275 K at $200\text{--}300\text{ }\mu\text{K s}^{-1}$ and then, from $T_c + 0.5\text{ K}$ to T_c at $5\text{--}10\text{ }\mu\text{K s}^{-1}$. Dry ice packed into an insulated box around the thermostat cooled the thermostat's unregulated outer shell to -20°C .

We made viscosity measurements by using a capacitance bridge to monitor the freely decaying torsion oscillations. The output of the bridge was of the form

$$\theta(t) = \theta_0 \sin(\omega t) e^{-\omega t D/2\pi}. \quad (3)$$

The initial amplitude θ_0 was typically 1 mrad and the frequency $\omega/2\pi$ was 5.4 Hz. The decrement D was determined by fitting an exponential function to the extrema of $\theta(t)$ for 50 periods. Typically, rms scatter in D was $\pm 0.2\%$.

Earlier viscosity measurements from this laboratory employed torsion oscillators with frequencies in the range 0.5 to 1.5 Hz. However, the larger viscosity of the polymer solution required us to raise the operating frequency to 5.4 Hz. At this higher frequency, the viscous penetration length δ was less than 2 mm, sufficiently smaller than the viscometer's dimensions to assure sensitivity of the decrement to the viscosity. The viscous penetration length δ is defined by

TABLE I. Nominal parameters for initial viscosity estimates.

Radius	R	15.19 mm
Half-height	h	7.61 mm
Moment of inertia	I	$3.652 \times 10^{-5} \text{ kg m}^2$
Period	$2\pi/\omega$	0.184 s
Density of fluid	ρ	1074 kg m^{-3}
Residual decrement	D_0	5×10^{-5}

$$\delta \equiv \frac{2\eta}{\rho\omega}, \quad (4)$$

where ρ is the solution's density. Other differences from previous viscosity measurements included the use of a programmable ratio transformer to automatically compensate for drift in the capacitance bridge's set point and a faster multimeter to record the extrema in the viscometer's torsional oscillations. The viscometer's characteristics are summarized in Table I.

III. RESULTS AND ANALYSIS

A. Culling of the data

We collected decrement data during three runs, each starting near room temperature and ending approximately 0.1 K below T_c . About 10% of the 2603 decrement measurements were culled because the standard deviation of the fit to Eq. (3) was too large. Usually, these measurements had been degraded by minor mechanical disturbances in the laboratory. Decrements measured at temperatures below T_c also were culled.

B. Conversion from decrement to viscosity

Our analysis accounted for the fact that the viscous penetration length δ was as large as 1.7 mm near T_c and was thus a significant fraction of the viscometer's inner radius R of 15 mm.

Newell and co-workers¹⁹ derived the equation of motion of an oscillating fluid-filled cylinder. It relates the viscosity to the decrement through a characteristic equation involving the sum of a series of hyperbolic tangents of complex elements (also see Ref. 20). It was too time consuming to use this exact result to reduce the decrement measurements. Instead we used an approximate working equation²⁰ to extract an initial estimate of the viscosity η from the decrement D . This working equation was correct to $O(\delta/R)^3$ and it contained the temperature-dependent parameters of the fluid density¹⁷ and the viscometer's dimensions. This initial estimate was then corrected by the ratio of the exact solution to the $O(\delta/R)^3$ estimate. This ratio, calculated for the nominal parameters, varied from 1.007 to 1.012 for our range of decrements. The sensitivity of this calculation scheme to the choice of nominal parameters was checked numerically and found to contribute less than 0.03% error to the final viscosity.

Because we had no independent means, such as turbidity measurements, for locating the critical temperature for each run, we defined T_c as the temperature of the cusp in a plot of the decrement as a function of the temperature. This defini-

tion is valid in the absence of gravitational stratification. (Stratification is important for the analysis of liquid-vapor critical point experiments.) In previous work on simple binary mixtures,¹ allowing T_c to be a free fit parameter yielded results consistent with defining T_c in this way.

C. Frequency and shear effects

The fluctuation relaxation time τ leads to a viscoelastic response for frequencies ω such that $\omega\tau > 1$. Bhattacharjee and Ferrell's theory²¹ for this response is consistent with the behavior of binary mixtures of small molecules.¹ Their theory predicts that the viscoelastic perturbation in our 5.4 Hz viscometer was less than 0.5% for $\omega\tau < 5$ at reduced temperatures greater than $\epsilon = 1.0 \times 10^{-3}$. For smaller reduced temperatures, we used this same theory in fitting our data, although the correction was always less than 4%.

Oxtoby's theory²² predicts that our maximum shear rate (0.46 s^{-1}) caused perturbations less than 0.5% for reduced temperatures above 1.5×10^{-4} . Data closer to T_c were excluded from the analysis.

We also considered the possible importance of other shear effects, including those known to exist in polymer solutions. One example was found by Takebe *et al.*,¹⁴ who measured shear-induced lowering of T_c in a mixture of polystyrene and polybutadiene dissolved in dioctyl phthalate. They found it to be much larger than that expected from similar measurements in binary mixtures of small molecules, even after correcting for the larger correlation length and viscosity in the polymer system. They reported a shift ΔT_c in the homogenization temperature of

$$\frac{\Delta T_c}{T_c} = -(2.6 \pm 0.6) \times 10^{-3} S^{0.50 \pm 0.02}, \quad (5)$$

where S is the shear rate in s^{-1} , and they proposed that the solution dynamics were governed by the intrinsic polymeric "reptation time" rather than by hydrodynamic interactions. Another example was found by Nakatani *et al.*,¹⁵ who recently measured the effects of shear rate on light scattering in a solution of polystyrene in dioctyl phthalate at room temperature. They interpreted their data in terms of a shear-rate-dependent spinodal temperature T_s with a shift ΔT_s given by

$$\frac{\Delta T_s}{T_s} = +1.57 \times 10^{-3} S^{3/2}. \quad (6)$$

We did not detect an effect of the size implied by Eq. (5) or Eq. (6). When we halved the oscillator amplitude at $\epsilon = 1.6 \times 10^{-3}$ no significant change in the viscosity was seen [e.g., Eq. (5) predicts a 1% change at this reduced temperature]. Also, Eqs. (5) and (6) predict that halving the shear rate shifts T_c by +0.14 and -0.09 K, respectively. To within ± 0.01 K, no such shift was detected. Apparently, the shear-rate effects seen by Takebe *et al.* or Nakatani *et al.* were not important in our measurements.

D. Miscellaneous corrections

The decrement of the empty viscometer was measured to be $D_0 = (5 \pm 1) \times 10^{-5}$ at 1.7 Hz, with no significant dependence on the temperature or the residual pressure of the sur-

rounding gas. (Because D_0 was due to the oscillator's solid components, its value was assumed to be independent of frequency.) The decrements for the filled viscometer fell between 0.019 and 0.029, and they were corrected by subtraction of D_0 .

Fluid in the expansion volume contributed a negligible amount to the total decrement. We calculated this amount by deriving the exact expression for the decrement per unit length in an infinite cylinder and then using this formula with the length of the liquid-filled portion of the expansion volume estimated from the liquid's density. The expansion volume was found to contribute 0.3% to the decrement at $\epsilon=0.1$ and only 0.08% near T_c . For comparison, recall that the rms scatter among decrement measurements was $\pm 0.2\%$.

As expected, the temperature of the sample lagged behind that of the thermistor embedded in the wall of the expansion volume. This caused a 0.7% discontinuity in the decrement when, at approximately 0.5 K above T_c , the temperature sweep rate was abruptly slowed from 200 to 10 $\mu\text{K s}^{-1}$. We therefore corrected the temperature data by an amount:

$$\Delta T = \dot{T} \tau_{\text{thermal}}, \quad (7)$$

with $\tau_{\text{thermal}}=300$ s, determined by the observed discontinuity. We checked this correction by estimating τ_{thermal} . We assumed that the thermal diffusivity of the solution was the same as that of pure diethyl malonate,²³ and we incorporated it into a simple model of the temperature field in the sample. Using the viscous penetration length as the characteristic length in the thermal model, we obtained 185 s as an estimate of the fluid's contribution to τ_{thermal} . The stainless steel walls of the viscometer contributed roughly another 100 s, making the total similar to the measured value. The correction for temperature lag had only a small influence on the fitted parameters.

Figure 2 shows our data and those of Gruner *et al.*¹⁷

E. Fitted equations

Close to T_c the viscosity of simple fluids is expected to have the form of Eq. (1), whereas far from T_c it has a non-critical temperature dependence $\eta_0(T)$. Although much work^{24,25} has been devoted to deriving an accurate expression for the viscosity at intermediate temperatures, to date such a "crossover" theory has been applied successfully only to pure fluids.

As was successfully done for simple binary mixtures,¹ we fitted the equation

$$\eta(t) = \eta_0(T) \epsilon^{-\gamma} F(\omega\tau) \quad (8)$$

to the viscosity data. The first order effects of viscoelasticity were accounted for by the function $F(\omega\tau)$, which is the ratio between the apparent viscosity and the zero-frequency viscosity and is known from theory.²¹

The data could not be adequately described using an Andrade ("Arrhenius") background for $\eta_0(T)$ in Eq. (8). Specifically, when

$$\eta(T) = A e^{B/T} \epsilon^{-\gamma} F(\omega\tau) \quad (9)$$

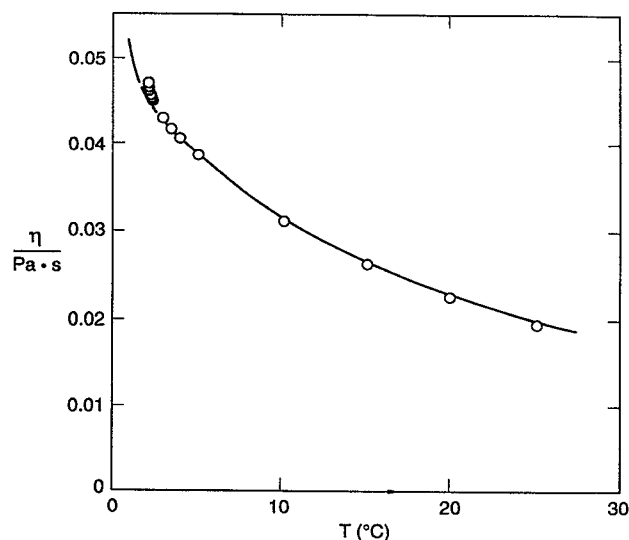


FIG. 2. The viscosity of the polymer solution as a function of temperature. The superposed data of Gruner *et al.* (Ref. 17) (circles) differ mainly in the critical temperature T_c , which is sensitive to trace amounts of dissolved water. Only 14 points from Gruner *et al.* are shown. Of these, the five closest to T_c were excluded from the analysis by the shear rate criterion.

was used, the systematic deviations of the measured viscosity from the best fit were as large as 2% far from T_c ($\epsilon=0.1$) and were typically 0.5% at temperatures closer to T_c .

Fits using a Vogel-Fulcher background in Eq. (8), namely

$$\eta(T) = A e^{B/(T-T_0)} \epsilon^{-\gamma} F(\omega\tau), \quad (10)$$

were more successful. Figure 3 shows the fitted function and the deviations for one run. The scatter and systematic deviations were similar for all three runs.

The fitted parameters for the three runs are given in Table II. Also included are the parameters resulting from fitting Eq. (10) to the data of Gruner *et al.*¹⁷ For consistency, these earlier data were restricted to the reduced temperature range $0.0015 < \epsilon < 0.1$, where the lower bound was determined by shear rate and the upper bound coincides with the present measurements.

IV. CONCLUSIONS

In spite of an 80-fold reduction in the shear rate and despite the use of an oscillating cup viscometer instead of a capillary viscometer, our results for the critical exponent for the viscosity agree with the data of Gruner *et al.* when the latter are analyzed in the same way. Figure 4 shows this

TABLE II. Fitted parameters for Eq. (10). Uncertainties are $\pm 1\sigma$.

	A (10^{-4} Pa s)	B (K)	T_0 (K)	100γ
Gruner <i>et al.</i>	7.6 ± 2.4	375 ± 69	179 ± 10	2.64 ± 0.28
Run No. 1	7.1 ± 2.1	424 ± 69	169 ± 9	2.66 ± 0.08
Run No. 2	8.3 ± 1.9	379 ± 50	177 ± 7	2.56 ± 0.10
Run No. 3	8.3 ± 0.8	372 ± 21	178 ± 3	3.07 ± 0.05

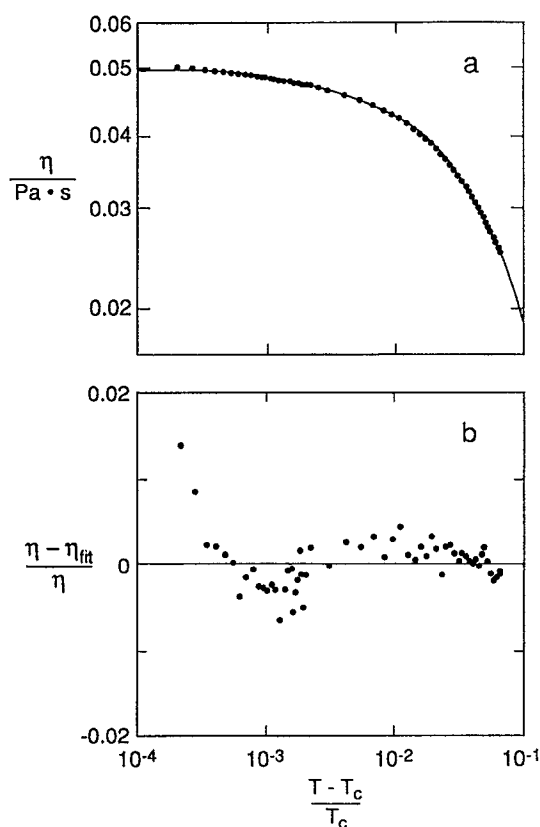


FIG. 3. (a) The viscosity of the polymer solution as a function of reduced temperature. The line is Eq. (10), which incorporates a Vogel–Fulcher background viscosity, in the limit of zero frequency. (b) Deviations of the data from Eq. (10), incorporating a Vogel–Fulcher background viscosity and the viscoelastic correction $F(\omega\tau)$ and fitted to the parameters in Table II.

agreement as well as the definite disagreement with the exponents found in binary liquids and pure fluids. (We do not know why the viscosity exponent for Run No. 3 differs from the others. However, this difference is a small fraction of the discrepancy between the polymer solution and the simpler fluids.) To emphasize the varied nature of the fluids, the experimental exponents y are plotted against the normalized slope of the background viscosity $d\eta_0/dT$.

The present experiment has ruled out two explanations for the anomalously lower viscosity exponents seen in polymer solutions. First, after eliminating the data close to T_c where shear thinning was expected, reduction of the shear rate by a factor of 80 from the measurement of Gruner *et al.* had no effect on the fitted exponent. Thus, shear thinning does not explain the lower exponents. Second, our oscillating cup viscometer and Gruner *et al.*'s capillary viscometer were very different instruments. The consistency of the results rules out any systematic error peculiar to either viscometer.

This consistency supports similar results found in capillary viscometer studies of other polymer solutions. Izumi *et al.*²⁶ measured the viscosity of solutions of polystyrene in cyclohexane and found $y = 0.029 \pm 0.003$. From the description of their experiment we estimate their maximum shear rate near T_c was 120 s^{-1} , typical of capillary viscometers. Hamano *et al.*⁷ also used a capillary viscometer to

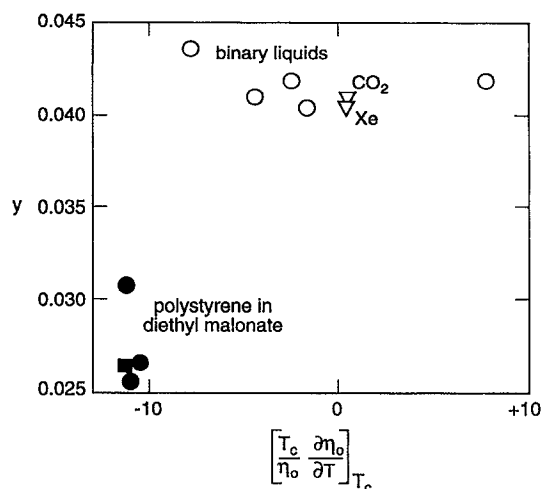


FIG. 4. The viscosity exponents measured in polystyrene plus diethyl malonate by the torsion oscillator (filled circles) and by a capillary viscometer [Gruner *et al.* (Ref. 17) filled square]. The disparity with the exponents obtained for other fluids can be seen. The open triangles are pure fluids (Ref. 2) and the open circles represent four binary mixtures of small molecules (Ref. 1) (methanol + cyclohexane was measured at both constant pressure and at constant volume). The horizontal axis indicates the temperature dependence of the background viscosity η_0 .

measure polydimethylsiloxane dissolved in diethyl carbonate and (in the limited range of $3.45 \times 10^{-4} < \epsilon < 1.77 \times 10^{-3}$) found $y = 0.028 \pm 0.001$. A correction for the shear rate raised this value to $y = 0.033 \pm 0.001$.

The apparent viscosity exponent might differ from those measured for simple fluids due to polydispersity. Debye *et al.*²⁷ pointed out that polydispersity can lead to difficulties in the determination of the critical temperature and concentration. For example, their transmission and light scattering measurements of T_c in a solution of polystyrene in cyclohexane disagreed by 0.7 K. However, we note that our critical temperature was determined to within a few millikelvin by the cusp in the decrement vs temperature curve, indicating a sharp transition. Also, determinations of static exponents in polymer solutions with comparable dispersion^{5–10} have yielded the expected Ising model exponents.

The apparent viscosity exponent might also be affected by an inappropriate functional form for the background viscosity η_0 . The Vogel–Fulcher expression used in Eq. (10) was chosen on empirical grounds. A shortcoming of this expression is that it does not explicitly account for the intramolecular contraction associated with the theta point of polymer solutions. As the solution cools, the polymer's intrinsic viscosity decreases, while the pure solvent's viscosity increases. This is an important effect because the viscosity of the present solution is approximately ten times greater than that of the solvent.²⁸ Due to this large ratio, knowledge of the concentration dependence of the viscosity at low concentrations²⁹ and the temperature dependence of the intrinsic viscosity³⁰ are inadequate for estimating $\eta_0(T)$ by extrapolating from the viscosity at lower concentrations.

The most interesting possibility for the viscosity exponent discrepancy between polymer solutions and simpler flu-

ids is that the two fluids are in different dynamic universality classes. This is strongly suggested by the present measurements and the similar results in other polymer solutions. However, this inference must be strengthened by a better characterization of the background viscosity, ideally, guided by an improved theory. Perhaps such characterization could be achieved by interpolation between measurements made at both above and below the critical concentration. Also, the temperature dependence of the background viscosity might be suppressed by measuring the viscosity at constant volume, as has been done for a simple binary liquid.¹ Another approach would be to use polystyrene of different molecular weights to change the distance between the theta and critical points.

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